

Investigation of Carbon Dioxide Methanation over Ceria Based Catalysts

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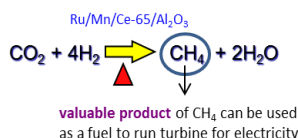
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Graphical abstract



Abstract

The recycling technology by the catalytic conversion is one of the most promising techniques for the CO_2 treatment of gas burning power plant flue gases. The methanation of CO_2 to valuable product of CH_4 shows significant environmental and economic benefits since the methane gas production can be used as a fuel to run the turbine for electricity generation. In addition, a highly basic catalyst such as ceria which has excellent redox properties is an effective material which could enhance carbon dioxide adsorption on the catalyst surface but has not been widely explored. Therefore, this research is focused on the development of ceria based catalysts by impregnating Ce to $\text{Ru/Mn/Al}_2\text{O}_3$ catalyst. From the catalytic testing, the addition of Ce to $\text{Ru/Mn/Al}_2\text{O}_3$ as based catalyst was found to be appreciably more active for promoting the CO_2 methanation reaction. Further investigation of the $\text{Ru/Mn/Ce/Al}_2\text{O}_3$ catalysts on the ceria loading and calcination temperature can significantly affect the catalytic performance. The optimum conditions were achieved with 65 wt% of cerium loading and calcination temperature of 1000°C which gave 97.73% CO_2 conversion with 91.31% of methane formation at reaction temperature of 200°C . Meanwhile, only 30.52% methane was formed from 30.72% CO_2 conversion over $\text{Ru/Mn-65/Al}_2\text{O}_3$ catalyst. The high activity of $\text{Ru/Mn/Ce-65/Al}_2\text{O}_3$ catalyst can be ascribed to its high surface area caused by the production of new active sites on the catalyst surface since the morphology of the catalyst had transformed to look like staghorn coral morphology. Furthermore, incorporating the Ce towards $\text{Ru/Mn-65/Al}_2\text{O}_3$ catalyst had induced the formation of Al_2O_3 with different crystalline phase (from rhombohedral to orthorhombic phase) and formation of MnO_2 and Mn_2O_3 .

Keywords: Methanation; coal burning power plant; carbon dioxide; flue gas; ceria

Abstrak

Teknologi kitar semula oleh penukaran bermangkin merupakan salah satu teknik yang paling berkesan untuk rawatan CO_2 pada gas serombong loji janakuasa pembakaran gas. Metanasi CO_2 kepada produk berharga CH_4 memberikan faedah penting kepada alam sekitar dan ekonomi kerana pengeluaran gas metana tersebut boleh digunakan sebagai bahan api untuk mengerakkan turbin bagi penjanaan elektrik. Di samping itu, pemangkin yang bersifat alkali tinggi seperti ceria yang mempunyai ciri-ciri redok yang sangat baik adalah bahan berkesan yang dapat meningkatkan penyerapan karbon dioksida pada permukaan mangkin tetapi tidak diterokai secara meluas. Oleh itu kajian ini memberi tumpuan kepada penyediaan mangkin berasaskan ceria yang diimpregnasikan oleh mangkin $\text{Ru/Mn/Al}_2\text{O}_3$. Dari ujian pemangkin, penambahan Ce sebagai bahan asas dalam $\text{Ru/Mn/Al}_2\text{O}_3$ didapati lebih ketara aktifnya bagi mempromosikan reaksi methanation CO_2 . Siasatan lanjut daripada pemangkin $\text{Ru/Mn/Ce/Al}_2\text{O}_3$ pada muatan ceria dan suhu pengkalsinan boleh memberi kesan yang ketara kepada prestasi pemangkin. Keadaan optimum telah dicapai dengan 65% berat muatan cerium dan suhu pengkalsinan 1000°C yang memberikan 97.73% penukaran CO_2 dengan 91.31% pembentukan metana pada suhu tindak balas 200°C . Sementara itu, hanya 30.52% metana terbentuk daripada 30.72% penukaran CO_2 oleh pemangkin $\text{Ru/Mn-65/Al}_2\text{O}_3$. Aktiviti yang tinggi oleh pemangkin $\text{Ru/Mn/Ce-65/Al}_2\text{O}_3$ disebabkan oleh kawasan permukaan yang tinggi hasil pembentukan tapak aktif baru pada permukaan mangkin kerana morfologi pemangkin telah berubah membentuk morfologi karang bertanduk rusa. Tambahan pula, pengabungan Ce terhadap pemangkin $\text{Ru/Mn-65/Al}_2\text{O}_3$ telah mendorong pembentukan Al_2O_3 dengan fasa kristal yang berbeza (dari rombohedral ke fasa ortorhombik) dan pembentukan MnO_2 dan Mn_2O_3 .

Kata kunci: Metanasi; loji kuasa pembakaran arangbatu; karbon dioksida; gas serombong; ceria

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1.0 INTRODUCTION

According to United Nations Development Report (2007), Malaysia ranked as the 26th largest greenhouse gases emitters with

the population over 27 million people. The major contributor of greenhouse gases is from power plant station since, the chemical composition of Connaught Bridge Burning Power Plant (Selangor, Malaysia) flue gases contained mainly of carbon

dioxide and water vapour. This showed that removing CO₂ gases from that type of plant is very important for maintaining a green environment. Therefore, the recycling technology by the catalytic conversion is one of the most promising techniques for the CO₂ treatment of gas burning power plant flue gases since the production of CH₄ can also be used as a fuel to run turbine for electricity. By recycling the CO₂ via this technique, the amount of natural gas needed for the combustion in a gas turbine can be reduced as well as CO₂ emissions. In order for this method to be effective, the production of catalysts and its behaviour should be investigated further.

The current technologies that has been investigated by many researchers for the treatment of carbon dioxide in power plant flue gases is Integrated Gasification Combined Cycle (IGCC) which involved high maintenance fees which is not cost effective.¹ In fact, there is no method applied to remove CO₂ in gas power plant flue gases and also there is no research done that used catalyst under this condition. Thus, a new technology that is the catalytic conversion method made from ceria, CeO₂ catalyst is introduced in this research.

Many researchers prefer to use Ni-based alumina supported system which is the traditional catalyst used for methanation.²⁻⁴ One of the reasons is because Ni is cheap and is proven to be able in producing high CO₂ conversion only at higher reaction temperature. However, the drawback of Ni catalyst is to produce high CO₂ conversion at possible low reaction temperature and its reproducibility properties. This is agreed by Wan Azelee *et al.*⁵ in his research using Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst calcined at 400°C. After underwent 4th test of reproducibility testing, Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst calcined at 400°C gave only 26.17% CO₂ conversion compared to the fresh catalyst which was 43.60% at reaction temperature 200°C. Therefore, a new catalyst that have potential to convert CO₂ to CH₄ at lower reaction temperature need to be found and therefore manganese was chosen as an alternative methanation catalyst.

Research done by Seok *et al.*⁶ had proved that the presence of manganese improves the stability and durability of catalysts in CO₂ reforming of methane. The addition of Mn to Ni/Al₂O₃ promoted the adsorption of CO₂ by forming the carbonate species and it was responsible for suppression of carbon deposition over Ni/MnO-Ni/Al₂O₃ catalyst. Other research done by Li *et al.*⁷ showed that when manganese was doped in appropriate amount, it caused disorder in the spinal structure of metal surface and enhanced the catalytic activity of the reactive species.

Besides, the Ru/Mn is an active catalyst for methanation process but not cost effective material because of the expensiveness of Ru and therefore hardly applied for practical. To overcome this problem, we have used the ceria as based catalyst so that the usage of Ru can be reduced and the methanation activity can be improved.

Currently, ceria is known as sulphur resistant catalyst and widely being used as carrier due to its unique acid–base and redox properties.⁸ It is well known that ceria can affect the thermal and structural stability of the catalyst support, the dispersion of supported metal and the decrease of carbon formation on the catalyst surface.^{8,9} In addition, a highly basic catalyst such as CeO₂ is proposed to enhance carbon dioxide adsorption and chemisorptions on the catalyst surface. It has excellent redox properties owing to the very fast reduction of Ce⁴⁺/Ce³⁺, which is associated with the formation of oxygen vacancies at the surface.¹⁰ However, the pure ceria hardly produced high activity of CO₂ methanation, therefore, the addition of ceria to Ru/Mn/Al₂O₃ catalyst was prepared. The structure, physicochemical properties and catalytic activity of the catalyst was investigated intensively.

■2.0 EXPERIMENTAL

2.1 Preparation of Catalysts

All the catalysts were prepared by aqueous incipient wetness impregnation method. 5 g of Ce(NO₃)₂·2H₂O obtained from MERCK was dissolved in small amount of distilled water. Mixed catalyst solution was prepared by mixing an appropriate amount of second or third metals such as Ru and Mnnitrate salts (Sigma Aldrich) with Ce(NO₃)₂·2H₂O solution according to its ratio. A homogeneous mixture was obtained by electromagnetic stirring at room temperature for 30 minutes. Alumina beads with diameter of 3 mm were used as support material in this study. The support was immersed into the catalysts solution until the solution was evenly absorbed on the surface of the support. The coating process was repeated three times with drying at ambient temperature for every coating process. It was then aged inside an oven at 80–90°C for 24 hours followed by calcinations using a furnace in the air atmosphere at 1000°C for 5 hours using a ramp rate of 10°C/min to remove all the metal counter ions and water present in the catalyst. Lastly, the sample was labelled as Ru/Mn/Ce-65/Al₂O₃ denoting there is 65 wt% of Ce, 30wt% of Mn and 5 wt% of Ru. Similar procedure was repeated for the Ru/Mn-65/Al₂O₃ catalyst which is Mn content is 65 wt%.

2.2 Characterization

The prepared catalyst undergoes several characterization techniques to study its chemical and physical properties. The structure of the catalyst was determined by X-Ray Diffraction (XRD) using Cu K α radiation ($\lambda=1.54060$ Å). Data was collected over the range of 2θ from 20 to 80° and analyzed by a PC interfaced to the diffractometer using software called Diffra Plus. Field Emission Scanning Electron Microscopy (FESEM) analysis was measured using a Ziess Supra 35VP FESEM with the energy of 15.0 kV couple with Energy Dispersive X-Ray (EDX) analyzer in order to determine the morphology and elemental composition of the catalyst. The sample was bombarded using an electron gun with a tungsten filament under 25 kV resolution to get the required magnification image. N₂ adsorption/desorption isotherm (NA) analysis of the catalyst was obtained using Micromeritics ASAP 2010 volumetric adsorption analyzer at -196°C. Prior to the measurement, the calcined catalysts were degassed at 120°C overnight.

2.3 Catalytic Activity Measurement

The catalytic CO₂ methanation reaction was performed under atmospheric pressure in a fixed micro reactor and analyzed via online Fourier Transform Infra-Red (FTIR) Nicolet Avatar 670 DGTS. The supported catalyst was placed in the middle of the glass tube made of Pyrex glass with diameter of 10 mm and length of 520 mm. It was then secured with glass wool at both ends. The reaction gas mixture consisting of CO₂, H₂, N₂, O₂ (10/40/39/11) was passed continuously through the catalyst and was heated in an isothermal tube furnace. The total flow rate was set to 100 mL/min, while the weight hourly space velocity was kept fixed at 636 mLg⁻¹h⁻¹. The feed gas flow rate was adjusted with a mass flow controller and the reaction temperature was performed from 60 up to 300°C with the increment temperature rate of 5°C/min. Off line Gas Chromatography (GC) analysis (Hewlett Packard 6890 Series GC System) was done to determine the yield of CH₄ gas due to the low sensitivity of FTIR spectroscopy towards the stretching band of CH₄.

Table 1 Texture and composition analysis towards Ru/Mn/Al₂O₃ and Ru/Mn/Ce/Al₂O₃ catalysts prepared by wetness impregnation method and calcined 1000°C

Catalysts	Ce loading (wt.%) ^a	Mn loading (wt.%) ^a	Ru loading (wt.%) ^a	BET Surface Area (m ² /g)	Average Pore Diameter (nm)	Cryst. Size (nm) ^b
Ru/Mn-65/Al ₂ O ₃	-	65	35	8.52	78.14	102
Ru/Mn/Ce-65/Al ₂ O ₃	65	30	5	47.65	23.90	86

^a Loading from Energy Dispersive X-Ray (EDX) analysis^b Crystallite Size data calculated by Scherer Equation

3.0 RESULTS AND DISCUSSION

3.1 Characterization

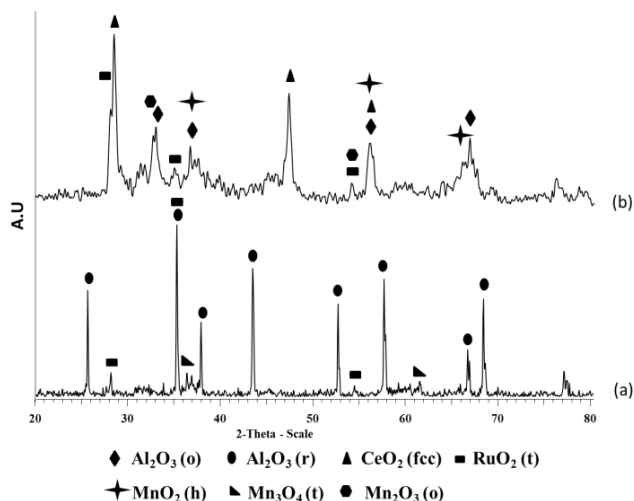
In this research, the content of catalyst was confirmed by Energy Dispersive X-Ray (EDX) analysis and is summarized in Table 1. The result was taken before the catalyst was calcined at 1000°C for 5 h. It can be seen that the ratio obtained from the EDX analysis was almost an equal value as stated in the catalyst ratio. Meanwhile, the physicochemical properties of the prepared catalysts are also listed in Table 1.

It is clearly observed that by promoting the ceria towards Ru/Mn/Al₂O₃ as based catalyst has a great influence on the BET surface area and average pore diameter. The BET surface area was increased remarkably from 8.52 to 47.65 m²/g, while pore diameter was decreased from 78.14 to 23.90 nm over Ru/Mn-65/Al₂O₃ and Ru/Mn/Ce-65/Al₂O₃ catalysts, respectively. This result indicates that the addition of Ce towards Ru/Mn/Al₂O₃ catalyst leads to the production of new active sites and hence increases its surface area.

Furthermore, the XRD analysis of Ru/Mn-65/Al₂O₃ revealed the rhombohedral (h) of Al₂O₃ at 2θ values of 35.131° (I₁₀₀), 43.329° (I₉₆), 57.410° (I₉₁), 25.550° (I₆₈), 68.089° (I₅₂), 52.475° (I₄₇), 37.323° (I₄₆) and 66.398° (I₃₅). It was transformed to the orthorhombic (o) Al₂O₃ at 2θ of 67.253° (I₁₀₀), 34.522° (I₈₀), 45.546° (I₈₀) and 38.993° (I₅₀) after the addition of ceria. It was probably due to the interstitial site that occurred in the structure of Ru/Mn-65/Al₂O₃ whereby some of the cerium atoms had occupied the space in the crystal lattice of Al₂O₃ thus changed the phase structure.^{11,12}

The peaks assigned to the tetragonal RuO₂ remained similar at 2θ values of 54.965° (I₅₄) and 35.051° (I₇₇). However, the peak of RuO₂ tetragonal phase at 28.124° (I₁₀₀) was broader due to the sharing of peaks with face center cubic of CeO₂ was also observed at 28.548° (I₁₀₀). Another two peaks of CeO₂ was at 2θ of 56.344° (I₃₅) and in the enveloped of Al₂O₃ peaks at 2θ of 47.485° (I₄₇).

Furthermore, the manganese oxide species was appeared in the form of tetragonal Mn₃O₄ over Ru/Mn-65/Al₂O₃ catalyst and detected at 2θ values of 61.872° (I₆₀). However, the pattern shows a very small peak which was hardly distinguished from the background noise. The overlapping of Mn₃O₄ diffraction peaks with those of the support peaks at 2θ of 36.466° (I₁₀₀) also occurred. Conversely, manganese oxide species detected over Ru/Mn/Ce-65/Al₂O₃ catalyst was in the form of hexagonal MnO₂ (2θ of 56.029°, 37.121° and 66.763°) and orthorhombic Mn₂O₃ (2θ of 32.921° and 55.141°).

**Figure 1** XRD diffractograms of a) Ru/Mn-65/Al₂O₃ and b) Ru/Mn/Ce-65/Al₂O₃ catalysts calcined at 1000°C for 5 h

FESEM images of Ru/Mn-65/Al₂O₃ and Ru/Mn/Ce-65/Al₂O₃ catalysts calcined at 1000°C are displayed in Figure 2. Generally, all the particles from both images are aggregated and agglomerated each other on the catalyst surface to form rough surface morphology. However, the catalyst with ceria addition (Figure 1b) showed slight different morphology which is like staghorn coral morphology. It branches out to look like deer antlers on the surface of the. Such morphology will provide the space for the access of active metal components to attract CO₂ and H₂ molecules on the catalyst surface. Therefore, the surface area obtained from nitrogen adsorption analysis over Ru/Mn/Ce-65/Al₂O₃ catalyst is much higher than catalyst without ceria.

It can be suggested that the characteristic obtained from NA, FESEM and XRD analysis after promoting the ceria to Ru/Mn-65/Al₂O₃ as based catalyst would help the increasing of CO₂ methanation activity.

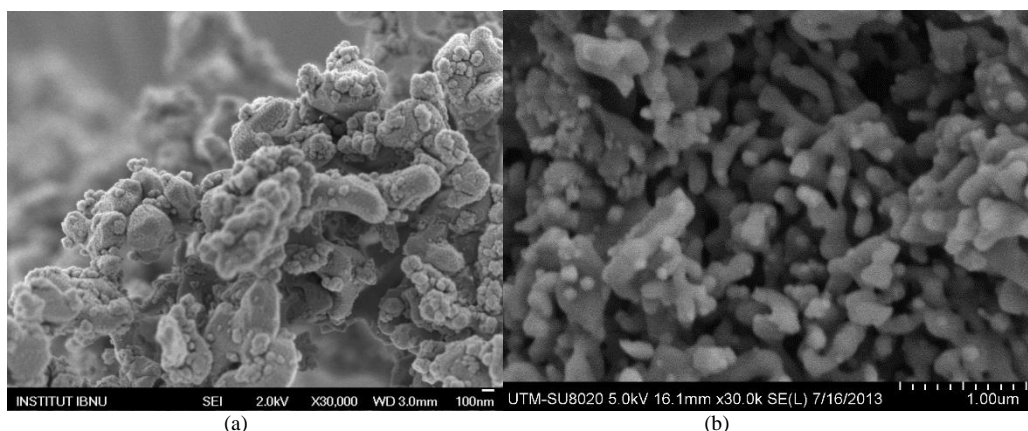


Figure 2 FESEM micrographs of fresh (a) Ru/Mn-65/Al₂O₃ and (b) Ru/Mn/Ce-65/Al₂O₃ catalysts calcined at 1000°C for 5 hours with magnification 30000X

3.2 Catalytic Performance

In this study, ceria was added to the Ru/Mn-65/Al₂O₃ catalysts to investigate the effect of ceria on catalytic CO₂ performance. Prior to the start of testing, the prepared catalyst was preheated for half an hour at 100°C. From Table 2, the Ru/Mn-65/Al₂O₃ catalyst achieved maximum CO₂ conversion at reaction temperature of 300°C with 51.10%. After the addition of ceria to the Ru/Mn-65/Al₂O₃ catalyst to form Ru/Mn/Ce-65/Al₂O₃, the activity was increased to 75.43% conversion at similar reaction temperature. It showed that the presence of ceria had improved the performance of Ru/Mn catalyst.

Table 2 Percentage conversion of CO₂ from methanation reaction over various Ru/Mn/Al₂O₃ with or without ceria calcined at 1000°C for 5 h

Catalysts	Reaction Temperature/ % CO ₂ Conversion		
	100°C	200°C	300°C
Ru/Mn-65/Al ₂ O ₃	6.81	18.23	51.10
Ru/Mn/Ce-65/Al ₂ O ₃	10.53	25.44	75.43

3.2.1 Robustness Testing

Before the investigation to optimization of Ru/Mn/Ce-65/Al₂O₃ catalyst, the robustness of the prepared catalysts was studied. The robustness testing was performed on stream continuously for 20 h at reaction temperature of 300°C. Figure 3 shows the percentage of CO₂ conversion as a function of reaction time over Ru/Mn/Ce-65/Al₂O₃ and Ru/Mn-65/Al₂O₃ catalysts.

It can be seen that the conversion of CO₂ over Ru/Mn-65/Al₂O₃ increased for the first 10 h with maximum conversion of 78.32% and started to decrease gradually after that. In contrast, the catalyst modified with ceria, Ru/Mn/Ce-65/Al₂O₃ exhibited good stability under the present operating condition. For first hour reaction time, the Ru/Mn/Ce-65/Al₂O₃ catalyst managed to convert 98.83% CO₂ and gradually increased until achieved 100% conversion at fifteen hours reaction time. After fifteen hour onwards, the catalyst was stable in terms of activity whereby the CO₂ conversion was constant at 100%.

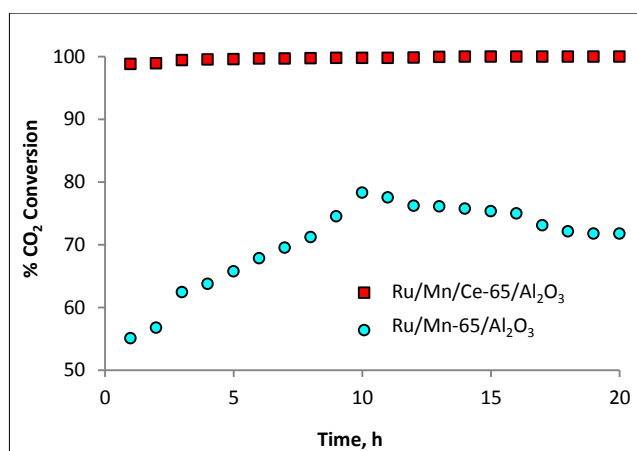


Figure 3 Robustness testing at reaction temperature of 300°C over Ru/Mn/Ce-65/Al₂O₃ catalyst calcined at 1000°C for 5 h

Therefore, the Ru/Mn/Ce-65/Al₂O₃ catalyst was categorized as a robust catalyst and was further optimized for several parameters such as different reduction temperatures, different calcination temperatures and ratios of the based/dopant catalyst. This process is important to obtain the best optimize condition towards the Ru/Mn/Ce-65/Al₂O₃ catalyst in order to get a great catalytic activity.

3.2.2 Effect of Reduction Pretreatments

In this section, catalytic performance of Ru/Mn/Ce-65/Al₂O₃ was studied by varying the pretreatment condition before start the CO₂/H₂ reaction. Prior to the start of testing, all the prepared catalysts were underwent air pretreatment at 100°C for 30 minutes. The reason to preheat the catalyst is to activate the catalyst as well as to remove the moisture in the catalyst. In this research, Ru/Mn/Ce-65/Al₂O₃ catalyst also underwent pretreatment in the presence of H₂ gas (40 mL/min) at temperature of 100 or 300°C for half an hour which was under reduction condition. As such, the entire active sites on the surface of the catalyst will be reduced to lower oxidation number or to metallic state consequently increased its catalytic activity. The catalyst was also pretreated in the presence of O₂ at 300°C as in Figure 4.

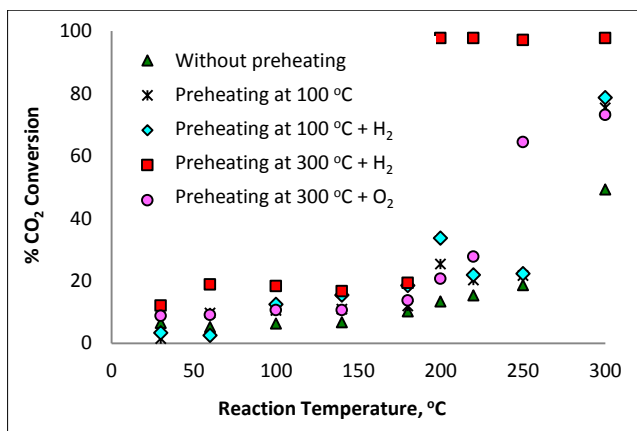


Figure 4 Catalytic performances of CO₂ conversion from methanation reaction over Ru/Mn/Ce-65/Al₂O₃ catalyst calcined at 1000°C with different pretreatments

The catalyst with preheating at 100°C for 30 mins was already discussed in Section 3.2 above. The CO₂ conversion over this condition achieved 25.44% at reaction temperature of 200°C which was increased slightly compared to the catalyst without preheating (13.41%). Furthermore, the CO₂ conversion at similar reaction temperature was rose notably from 33.75 to 97.73% with the increasing of pretreatment temperature from 100 to 300°C in the presence of H₂. This result shows that the reduction pretreatment will cause the reorganization of the surface structure as claimed by Kim *et al.*¹³ where the C-O bond was weakened by the active oxygen on NiO, preferentially reacts with H₂. The surface carbon intermediate facilitated by NiO was then easily hydrogenated to produce methane. Meanwhile, pretreatment with O₂ just gave similar result to that preheated at 100°C.

3.2.3 Effect of Calcination Temperatures

To study the effect of calcination temperatures towards ceria catalyst in this research, the alumina supported ceria catalysts were calcined at 400, 900, 1000 and 1100°C. The trends of its catalytic performance are shown in Figure 5.

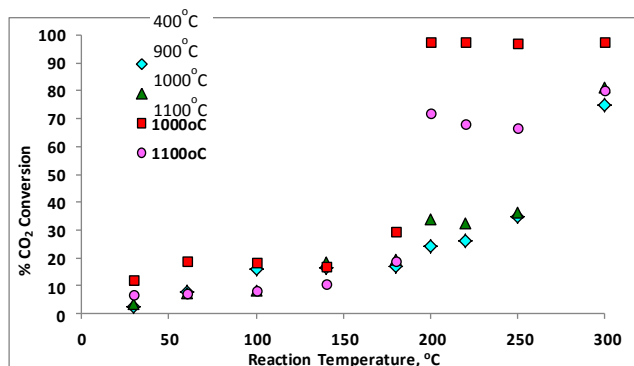


Figure 5 Catalytic performance of CO₂ conversion from methanation reaction over Ru/Mn/Ce-65/Al₂O₃ catalyst calcined for 5 hours at different calcination temperatures

The CO₂ conversion of ceria impregnated by Ru/Mn/Al₂O₃ catalyst increased apparently with the increase of calcination temperatures until 1000°C and decreased back at 1100°C. It

showed that the calcination temperature of 1100°C was not suitable where it seems that the catalyst was not stable and showed low CO₂ conversion at reaction temperature of 200°C (72.05%) compared to the catalyst that was calcined at 1000°C. The best calcination temperature of 1000°C over Ru/Mn/Ce-65/Al₂O₃ gave highest CO₂ conversion of 97.73% at reaction temperature of 200°C.

3.2.4 Effect of Ce Loading

In order to study the effect of ceria on catalytic performance, the CO₂ conversion was performed over Ru/Mn/Ce-65/Al₂O₃ catalyst by varying the ceria content from 60 to 85 wt%. The trend of CO₂ performance towards effect of ceria loading is depicted in Figure 6.

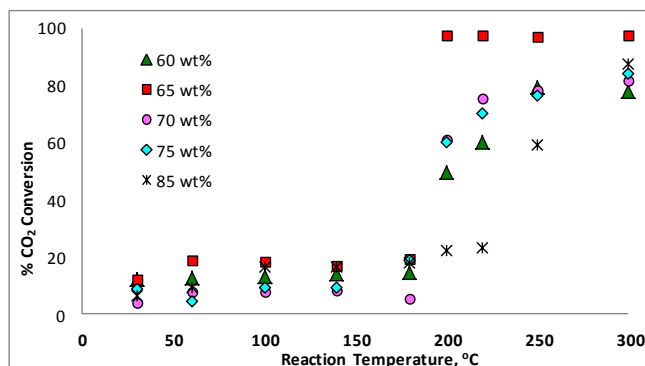


Figure 6 Catalytic performance of CO₂ conversion from methanation reaction over Ru/Mn/Ce-65/Al₂O₃ catalyst calcined at 1000°C for 5 hours with various cerium loadings

It was clear that the presence of ceria had significant influence on the CO₂ conversion. The CO₂ conversion increased sharply from 49.43% to approximately 100% conversion at reaction temperature of 200°C with the ceria loading from 60 to 65 wt%. However, the promoting effect of CO₂methanation would be unremarkable when further increase the ceria loading from 65 to 85 wt%. It clearly showed that an appropriate amount of ceria would increase the catalytic activity of the catalyst and surface basicity as well. Conversely, the excessive addition of ceria retarded the CO₂ conversion due to the enrichment of ceria on the catalyst surface which will cause the agglomeration to occur. Therefore, it can be concluded that the optimum loading for ceria content is 65 wt%.

3.2.5 Effect of Ceria Addition towards Methane Formation

Tables 3 shows the testing results of CO₂/H₂methanation reaction over Ru/Mn/Al₂O₃ catalyst with or without ceria tested at optimum operating conditions. Both catalysts were calcined at 1000°C for 5 h and pretreated at 300°C for 30 mins in the presence of H₂. Overall, the CH₄ content was increased as temperature was increased.

It can be seen that, only 30.52% of methane was formed over Ru/Mn-65/Al₂O₃ catalyst at studied temperature of 200°C. However, the methane production was increased to 91.31% over 97.73% CO₂ conversion when ceria was added to the catalyst to form Ru/Mn/Ce-65/Al₂O₃ catalyst at similar reaction temperature. The other 6.42% of CO₂ conversion was probably formed the product of CO.

Table 3 Methane formation over various Ru/Mn/Al₂O₃ with or without ceria calcined at 1000°C for 5 h, pretreated at 300°C for 30 mins in the presence of H₂

Catalysts	Reaction Temperature		
	100°C	200°C	300°C
	% Conversion of CO ₂		
Ru/Mn-65/Al ₂ O ₃	0	30.52	37.41
Ru/Mn/Ce-65/Al ₂ O ₃	8.7	91.31	66.55

■4.0 CONCLUSION

The modification of the Ru/Mn-65/Al₂O₃ catalyst by adding the ceria as a based could change the structure of the catalyst. The phase transformation of crystalline to polycrystalline state cause the increasing of catalyst surface area, giving smaller particles size, reducing the average pore diameter of the catalyst as well as change the morphology to staghorn coral like morphology. Those properties would increase the catalytic activity over Ru/Mn/Ce-65/Al₂O₃ catalyst to 97.73% as well as 91.31% of methane was formed from the reaction at reaction temperature 200°C. The catalyst promoted by ceria exhibited excellent stability for 20 h on stream without deteriorate. The operating condition of 65 wt% of ceria, calcined at 1000°C for 5 h, and pretreated with H₂ at 300°C for 30 mins would be the ideal conditions for the catalytic methanation over Ru/Mn/Ce-65/Al₂O₃ catalyst.

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